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Performance Evaluation of Active and Non-active Electrodes for Doxorubicin Electro-oxidation

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Abstract

Electrochemical remediation is an innovative technique that utilizes electro-oxidation reactions to degrade micropollutants such as doxorubicin (DOX) that is a drug widely used to treat many types of cancer, and it is present in hospital effluents. The aim of this work is to evaluate the efficiency of active and non-active electrodes in DOX degradation during electrochemical treatments. AuO-TiO2@graphite, a nanostructured electrode, and BDD, a commercial electrode, were used as active and non-active electrodes respectively. DOX treatments were realized at concentration of 1.25 mmol L-1 in medium with 10 mmol L-1 NaCl as support electrolyte. Studies were realized in 5 V of voltage source. Results: The treatment of DOX with BDD promoted 100% of DOX degradation in 20 min, while the same result was obtained for the AuO-TiO2@graphite in 40 min of treatment. Also, the modified electrode presented an energy expenditure of 1.12 kWh m-3 and the BDD achieved 0.462 kWh m-3. Thus, the active and non-active electrodes were efficient to promote DOX degradation, and the BDD, the non-active electrode demonstrated a better performance.

Keywords: Eletro-Oxidadion, Modified Graphite Anodes, BDD, Doxorubicin, Micropollutants

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1. Introduction

Electrochemical remediation is an innovative technique that utilizes oxidation and reduction reactions to remove organic compounds commonly presents in pharmaceutical, agroindustrial, and textile effluents. This methodology has environmental compatibility, being a sustainable method that does not use polluting chemical compounds. Moreover, it has high energy efficiency, easy handling and application safety [1–3].

The electro-oxidation (EO) occurs principally by the water electrolysis that generates •OH with standard reduction potential (E° (OH / H2O) = 2.80 V / EPH) that reacts non-selectively to the decomposition of various organic pollutants [4].

Doxorubicin (DOX) is an anthracycline widely used in antineoplastic therapy of acute lymphoblastic and myeloblastic leukemia, renal and soft tissue cancer such as breast and ovarian cancer [5]. Studies show significant concentration (above 1 $\mu g L^{-1}$) of DOX in hospital effluents, which demonstrates the need for effective technologies that promote its degradation [6].

Depending on the material constitution of the anode, the contaminant degradation by EO is accomplished through different reaction with active electrode (AE) (Figure 1, reactions 1, 4, 5 and 6) and non-active electrode (NAE) (Figure 1, reactions 1, 2 and 3) [7].

The main AE anodes are platinum (Pt), titanium (Ti), iridium dioxide (IrO_2), ruthenium dioxide (RuO_2), commercial dimensionally stable electrode (DSA®) formed by titanium metal with a thin layer of IrO_2 or RuO_2 and graphite [1, 3]. On the other hand, the NAE anodes are mainly formed by lead dioxide (PbO_2), tin dioxide (SnO_2), commercial Ebonex® electrode, composed of Ti_4O_7 and boron-doped diamond (BDD) (Supplementary Material 1) [1, 4, 8].

BDD is the most potent NAE anode known, mainly due to its high O_2 evolution potential that can reach 2.6 V / EPH. In addition to the large potential window, BDD has chemical stability, high corrosion resistance and low background currents [1, 4].

The graphite is an AE that can improve its effectiveness with the addition of nanostructured metal oxides such as titanium dioxide with gold oxide (AuO-TiO_2@graphite). This modification increases the conductivity and surface area, which enables greater formation of •OH and increases the adsorption of polluting compounds [13]. Thus, the objective of this study is to compare a nanostructured graphite electrodes and the BDD in the DOX degradation.

2. Methods

2.1. Sample

Doxorubicin hydrochloride (CAS Number 25316-40-9, European Pharmacopoeia reference standard) was purchased from Sigma-Aldrich. DOX solutions were prepared at the concentration of 1.25 mg L^{-1} in Milli-Q water purified water (Millipore S.A) with 10 mmol L^{-1} of NaCl as supporting electrolyte. The solutions were protected from light.

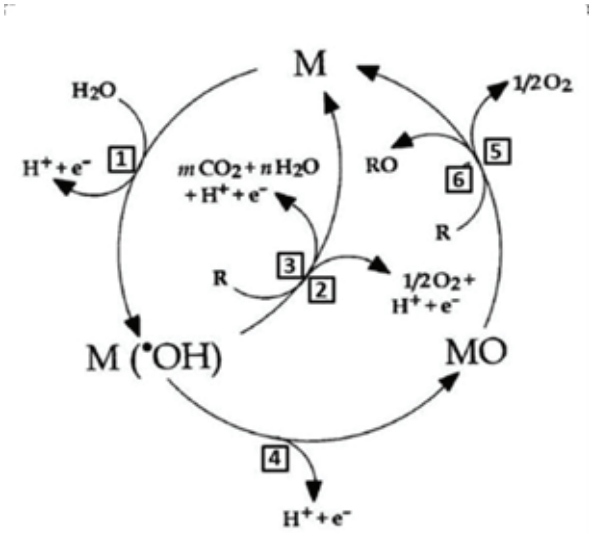

Figure 1: Electrochemical remediation by electro-oxidation with active (reações 1, 4, 5 e 6) and non-active (reações 1, 2 e 3) anodes [7].

2.1.1. Electrochemical treatment with AuO-TiO2@graphite

DOX electrochemical degradation was performed in a 5 mL capacity electrochemical cell. Pt wire was used as a cathode and the anode efficiency was evaluated with graphite@AuO-TiO_2. Assays were conducted using 3 ml DOX solution with Milli-Q purified water (conductivity <0.1 µS cm^{-1}) Millipore S.A., Molsheim, France with an addition of 10 mmol L^{-1} of NaCl.

A 5.0 V voltage controlled by a tensiometer was applied to an adjustable DC power supply (HF-30035, Hikari, Sao Paulo, SP, Brazil) for 0 to 120 minutes. DOX degradation was monitored by a UV-Vis spectrophotometer (Chemisch Scientific Instruments, model Q798U2VS) coupled to the Unique Application Software (S2100 UV / Vis Series). Spectra were scanned at 190 to 800 nm.

2.1.2. Electrochemical treatment with BDD

Electro-oxidation experiments were performed on a filter press electrochemical reactor (DiaClean®, WaterDiam) equipped with a commercial BDD anode (WaterDiam) and a stainless-steel cathode (AISI 304). The electrodes were circular with 78.5 cm^2 of geometric area and the distance between them in the reactor was 2 mm. The system was operated with 1000 mL of flow solution (400 mL min-1) using a peristaltic pump. The experiments were conducted in galvanostatic mode with the support of a DC power supply (FCC-3005D, Dawer) and a meter (ET-1400, Iminipo) was used to monitor the voltage. The sample was protected from light.

2.2. Energy Consumed

The energy consumption (*EC*, kWh m^{-3}) per volume of treated solution was obtained from Eq. 1, where E_{cell} is the average cell voltage (V), *I* is the applied current (A), *t* is the electrolysis time (hours), and $V_{reactor}$ is the volume of the treated solution (m^3).

$$EC(kWh\ m^{-3}) = \frac{E_{cell} I t}{V_{reactor}} \quad (1)$$

2.3. Results and discussion

The degradation of polluting compounds by electrochemical remediation using active or non- active anodes is an interesting strategy for water decontamination. This advance in electrochemical processes is related to the improvement of the materials that constitute the electrodes [1].

Comparisons of DOX degradation were evaluated using two different types of electrodes, the AE AuO-TiO_2@graphite [14], previously produced by Sanz-Lobón et al. [15], and the BDD [16 in preparation], the NAE most used in literature [1]. The Figure 2 shows the performance of these electrodes.

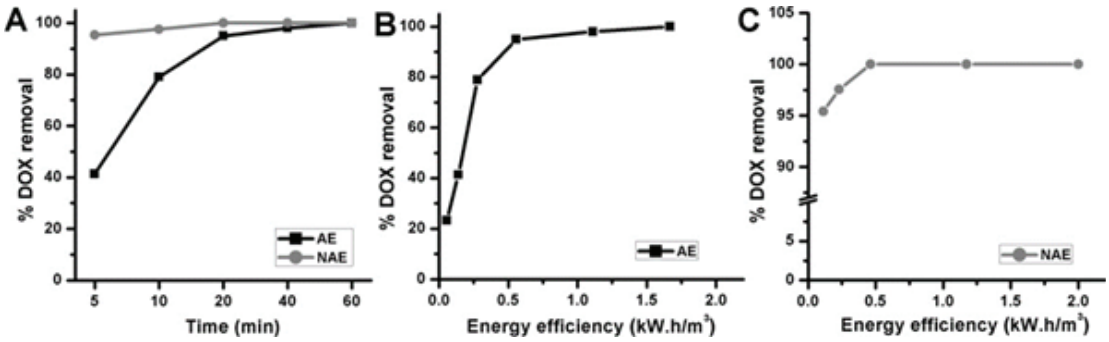

Figure 2: DOX degradation (A) and Energy efficiency (B and C) of active electrode (AE) AuO-TiO_2@graphite, and non-active electrode (NAE) BDD.

The DOX EO methods were efficient for both the nanostructured graphite electrode and the commercial BDD electrode. The AE promoted approximately 100% DOX degradation in 40 minutes of treatment. For NAE, nearly 95% of DOX removal was achieved after 5 minutes of electrolysis and approximately 100% after 20 minutes. The experiments were conducted in 5V and 1 mA (Figure 2A).

The ability of DOX degradation by electrodes is based on the materials capacity to produce strong oxidizers on its surface, such as OH [17, 18]. For both electrodes, high degradation efficiency was observed for the DOX solution with 10 mmol L-1 of

NaCl as supporting electrolyte, due to the production of chlorinated oxidants such as hypochlorous acid that has a high oxidizing power [18].

Due to the inherent variables of each methodology, the comparison of their performances was evaluated by energy efficiency, which takes into account the average cell voltage, the applied current, the volume of the treated solution and the electrolysis time. For the AE, the energy efficiency was 1.12 kWh m^{-3} and for the NAE, it was 0.462 kWh m^{-3} (Figure 2 B and C). Thus, the AE and NAE were efficient to promote DOX degradation, and the BDD, the NAE electrode presented better time of treatment and energy consumption. This characteristic is related to the formation of reactive BDD (•OH) with high oxidation capacity of organic compounds and low rate of parasite reactions [1].

Electrochemical remediation for antineoplastic drugs has been studied using different electrodes in order to investigate the best analytical performance for these assays (Table 1).

Table 1: Electrochemical degradation of antineoplastic drugs.

Antineoplastic	Method	Solution	Treatment time	Removal Percentage	Reference
DOX	BDD	1.25 mmol L^{-1} and 10 mmol L^{-1} NaCl	20 min	100%	This work
DOX	AuO-TiO2@graphite	1.25 mmol L^{-1} and 10 mmol L^{-1} NaCl	40 min	100%	This work
DOX	Fe-Ni bimetallic nanoparticles	100 mg L^{-1}	20min	84%	[19]
5-fluorouracil	Electro- fenton/ BDD/ carbon felt	0.1 mmol L^{-1} and 0.2 mmol L-1 Fe2+,	6 min	100%	[20]
Ifosfamide	EO/BDD/Stainless steel Ag/AgCl and0.1 mol L-1 KCl	0.19 mmol L^{-1} and 42 mM Na_2SO_4	240 min	86%	[21]
Imatinib	EO/BDD	50 mg L^{-1}	60 min	100%	[22]
Methotrexate	EO/BDD	50 mg L^{-1}	120 min	100%	[22]
Cyclophos-phamide	EO/BDD	50 mg L^{-1}	More than 300 min	100%	[22]

Thus, it is possible to observe that the electrochemical treatments proposed in this work for DOX degradation are in accordance with the literature and are presented as efficient strategies for the removal of pharmaceutical contaminants.

3. Conclusions

DOX is a drug widely used in antineoplastic therapies, which becomes a micropollutant in the effluents. Because of the need to treat this compound, EO with AuO-TiO2@graphite, an AE electrode and BDD, NAE anode were used, and both proved to be a viable alternative.

The treatments with NaCl promoted complete DOX degradation with BDD in 20 min, and the same result was achieved with AuO-TiO_2@graphite in 40 min of treatment. Also, a higher efficiency was attributed to the NAE electrode with energy consumption of 0.462 kWh m^{-3} and AuO-TiO_2@graphite of 1.12 kWh m^3. Thus, the proposed treatment process is useful for DOX degradation, and BDD was more efficient.

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Supplementary Material 1

References

[1] Sirés, I. and Brillas, E. (2012). Remediation of water pollution caused by pharmaceutical residues based on electrochemical separation and degradation technologies: A review. *Environ Internat*, vol. 40, pp. 212–229.

[2] Panizza, M. and Martinez-Huitle, C.A. (2013). Role of electrode materials for the anodic oxidation of a real landfill leachate – Comparison between Ti–Ru–Sn ternary oxide, PbO2 and boron-doped diamond anode. *Chemosphere*, vol 90, issue 4, pp. 1455–1460.

[3] Moreira, F.C., Boaventura, R.A.R., Brillas, E. *et al.* (2017). Applied Catalysis B Environmental Electrochemical advanced oxidation processes A review on their application to synthetic and real wastewaters. *Applied Catalysis B, Environmental*, vol. 202, pp. 217–261.

[4] Panizza, M.E. and Cerisola, G. (2009). Direct and mediated anodic oxidation of organic pollutants". *Chemical Reviews,* vol. 109, pp. 6541–69.

Anodes	Advantages	Disadvantages	Potential for O2 evolution (V/EPH*)
Active anodes			
Pt	Inert	Low O_2 evolution potential; High cost.	1, 6-1,9
Ti	Good stability	High cost	
IrO_2	Good conductivity; Good electrocatalytic activity.	Low stability	1,4-1,7
RuO_2	Good conductivity; Good electrocatalytic activity.	Low stability; May be corroded	1,4-1,7
DSA® - *Dimensionally Stable Anode*	Good evolution potential of O_2; Good current efficiency; Low cost.	Low lifespan; Lack of chemical stability	1,4-1,8
Graphite	Low cost; Easy handling; Great applicability	Corrosion at high stresses.	1,7
Non-active anodes			
PbO_2	High evolution potential of O_2; Good current efficiency; Low cost; Good current efficiency; Easy handling.	Pode sofrer corrosão e liberar íons Pb^{2+}; Tóxicos. May corrode and release Pb^{2+} ions; Toxic.	1,8-2,0
SnO_2	High electrical conductivity; High stability.	It loses effectiveness after a short period of use.	
Ebonex® - Ti_4O_7	High evolution potential of O2; Good current efficiency; Low cost; Good current efficiency; High chemical stability; Good corrosion stability; Good conductivity. Easy handling.	High cost.	1,7-1,8
Boron doped diamond	High evolution potential of O2; High chemical stability; Good conductivity; Good current efficiency; Inert under extreme conditions.	Very high cost.	2,2-2,6

Fonte: [3, 9, 10,11,12,] * EPH: eletrodo padrão de hidrogênio

[5] Palchik, V., Traverso, M. L., Colautti, M. *et al*. (2016). Oncology medications prescription in a cancer service: appropriateness to clinical practice guidelines. *Farmacia Hospitalaria*, vol 40, issue 6, pp. 491-495.

[6] Mahnik, S.N.; Lenz, K.; Weissenbacher, N., *et al* (2007). Fate of 5- fluorouracil, doxorubicin, epirubicin, and daunorubicin in hospital wastewater and their elimination by activated sludge and treatment in a membrane-bio-reactor system. *Chemosphere,* vol. 66, pp. 30–7.

[7] Marselli, B., Garcia-Gomez, J., Michaud, P. A., *et al* (2003). Electrogeneration of hydroxyl radicals on boron-doped diamond electrodes". *Journal of the Electrochemical Society*, vol 150, issue 3, pp. 150, 79–83.

[8] Farinos, R.M. and Ruotolo, L.A.M. (2017). Comparison of the electrooxidation performance of threedimensional RVC/PbO2 and boron-doped diamond electrodes. *Electrochimica Acta,* vol. 224, pp. 32–39.

[9] Ganiyu, S.O., Oturan, N., Raffy, S., *et al* (2016). Sub-stoichiometric titanium oxide (Ti4O7) as a suitable ceramic anode for electrooxidation of organic pollutants: A case study of kinetics, mineralization and toxicity assessment of amoxicillin. *Water Research*, vol 1, issue 6, pp.171-172.

[10] Montilla, F., Morallo, E., De Battisti, A. *et al* (2004). Preparation and characterization of antimony-doped tin dioxide electrodes. Part 2. XRD and EXAFS characterization. *Journal of Physical Chemistry B*, vol. 108, pp. 5044-5050.

[11] Cherevkoa, S., Geiger, S., Kasiana, O., *et al* (2015). Oxygen and hydrogen evolution reactions on Ru, RuO_2, Ir, and IrO_2 thin film electrodes in acidic and alkaline electrolytes: A comparative study on activity and stability. *Catalysis Today*, vol. 262, pp. 170-180.

[12] Särkkä, H., Vepsäläinen, M. and Sillanpää, M. (2015). Natural organic matter (NOM) removal by electro-chemical methods – A review. *Journal of electroanalytical chemistry*, vol. 755, pp. 100–108.

[13] Dunnill, C.W., Kafizas, A., and Parkin, I.P. (2012). CVD Production of Doped Titanium Dioxide Thin Films". *Chemical Vapor Deposition,* vol. 18, pp. 89-101.

[14] Moreno, E.K.G., Garcia, L.F., Lobón, G.S. *et al* (2019). Ecotoxicological assessment and electrochemical remediation of doxorubicin". *Ecotoxicology and Environmental Safety*, vol. 179, pp. 143–150.

[15] Sanz-Lobón, G., Yepez, A., Garcia, L.F., *et al* (2017). Efficient electrochemical remediation of microcystin-LR in tap water using de- signer TiO_2@carbon electrodes. *Sci Rep* Vol. 7, pp. 41326.

[16] Garcia, L.F., Moreno, E.K.G., Brito, L.B., *et al*. Electro-chemical doxorubicin removal on boron doped diamond: and effective technology to abate ecotoxicity. (In preparation).

[17] Mohora, E., Roncevic, S., Dalmacija, B., *et al* (2012). Removal of natural organic matter and arsenic from water by electrocoagulation/flotation continuous flow reactor. *J. Hazard. Mater, v*ol. 235–236, pp. 257–264.

[18] Salazar, C., Contreras, N., Mansilla, H.D., *et* al (2016). Electrochemical degradation of the antihypertensive losartan in aqueous medium by electro-oxidation with boron-doped diamond electrode. *J Hazard Mater*, vol. 319, pp. 84-92.

[19] Kadu, B.S., Wani, K.D., Kaul-Ghanekar, R., *et al* (2017). Degradation of doxorubicin to non-toxic metabolites using Fe-Ni bimetallic nanoparticles. *Chem Eng J*, vol. 325, pp. 715–724.

[20] Ganzenko, O., Oturan, N., Sirés, I. *et al.* (2018). Fast and complete removal of the 5-fluorouracil drug from water by electro-Fenton oxidation. *Environmental Chemistry Letters*, vol. 16, issue 1, pp. 1–6.

[21] Fabiańska, A., Ofiarska, A., Fiszka-Borzyszkowska, A. *et al.* (2015). Electrodegradation of ifosfamide and cyclophosphamide at BDD electrode: Decomposition pathway and its kinetics. *Chemical Engineering Journal*, vol. 276, pp. 274–282.

[22] Siedlecka, E.M., Ofiarska, A., Borzyszkowska, A.F., *et al* (2018). Cytostatic drug removal using electrochemical oxidation with BDD electrode: Degradation pathway and toxicity. *Water Research*, vol. 144, pp. 235- 245.